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XV.

CONTRIBUTION FROM THE SALISBURY LABORATORY OF THE WORCESTER POLYTECHNIC INSTITUTE.

ON THE FORMATION OF SUBSTITUTED BENZOPHENONES.

By George D. Moore and Daniel F. O'Regan.

The preparation of benzophenone by heating benzoic acid, benzol, and phosphorpentoxide in sealed tubes at 180–200° has already been described by Kollarits and Merz.* The same authors † have also shown that benzoic anhydride reacts, under similar conditions, in the same manner as benzoic acid. We have proved ‡ that not only benzoic acid, but also the three isomeric mono-nitro, chlor, and brom acids yield anhydrides as the first product of this reaction. In the present paper we will describe the preparation of the nitro, chlor, and brom benzophenones from these anhydrides.

I. *Action of Phosphorpentoxide upon Orthonitrobenzoic Anhydride in an Excess of Benzol.*

10 grams of orthonitrobenzoic anhydride, m.pt. 133°, prepared by boiling a benzol solution of the acid with phosphorpentoxide, were heated in a sealed tube with 15 grams phosphoric anhydride and 25–30 c.c. pure dry benzol at 150° for about four hours. A slight reaction takes place in the cold, as evidenced by the rapid blackening of the solid constituents of the mixture, although the benzol remains uncolored.

After heating, the dark-colored mother liquor was decanted from the black residue, decolorized by means of bone-black, and concentrated until, on cooling, crystals were deposited. These, after washing with pure benzol and drying between filters, showed a melting point of 132–133°. The body is therefore the unaltered anhydride.

The black residue was a hard, vitreous mass, which clung so tenaciously to the tube that it was necessary to crush the latter completely in order to separate them. The fragments were then pulverized in a mortar, extracted with dilute potash, washed clean, and boiled up with 150–200 c.c. of absolute alcohol under a reverse cooler. This alcoholic liquor gave, after treatment with bone-black and concentrating, a crystalline precipitate, which we purified with considerable difficulty as the quantity was exceedingly small. We finally succeeded in getting a sufficient amount of it of constant melting point (104–105°) for an analysis.

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* Zeitschr. für Chemie, 1871, p. 705. Ber. d. ch. G., V. 447. † *Loc. cit.*

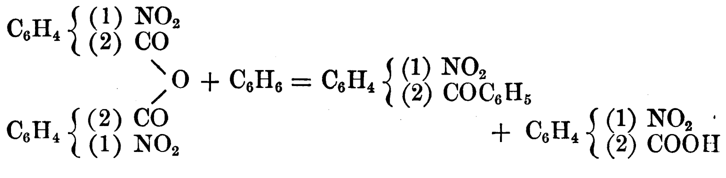
‡ These Proceedings, XXVII. 93.

0.1010 gr. substance gave 0.2537 gr. CO_2 and 0.0392 gr. H_2O.

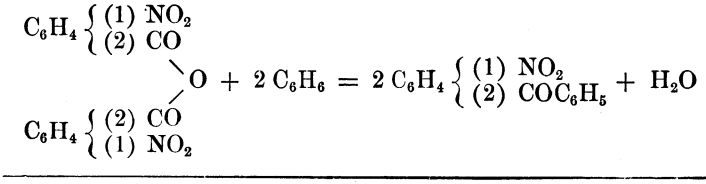
	Calculated for $C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(2)\ COC_6H_5.\end{matrix}\right.$	Found.
C	68.72	68.50
H	3.97	4.31

The yield is so small that we could not obtain a sufficient quantity to enable us to examine its properties as fully as we could wish. All attempts to increase the yield by varying the proportions, temperature, time of heating, etc., were without effect. Benzol takes up little or nothing from the raw product, and the same may be said of the other common solvents with the exception of boiling absolute alcohol. Dilute alkalies extract more or less orthonitrobenzoic acid. The concentrated alcoholic solution remains clear for several days, then manifests a slight turbidity, and finally deposits microscopic crystals. In several instances we have succeeded in obtaining only a thick syrup which could not be made to crystallize.

From the analysis of the substance and the method of its preparation we conclude that it is the orthonitrobenzophenone described by Geigy and Königs,* and interpret its formation by the following reactions: —



$$\begin{matrix} C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(2)\ CO\end{matrix}\right. & & \\ & \!\!\!>O + C_6H_6 = C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(2)\ COC_6H_5\end{matrix}\right. & \\ C_6H_4\left\{\begin{matrix}(2)\ CO\\(1)\ NO_2\end{matrix}\right. & & + C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(2)\ COOH\end{matrix}\right. \end{matrix}$$



$$\begin{matrix} C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(2)\ CO\end{matrix}\right. & \\ & \!\!\!>O + 2\,C_6H_6 = 2\,C_6H_4\left\{\begin{matrix}(1)\ NO_2\\(2)\ COC_6H_5\end{matrix}\right. + H_2O \\ C_6H_4\left\{\begin{matrix}(2)\ CO\\(1)\ NO_2\end{matrix}\right. & \end{matrix}$$

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* Ber. d. ch. G., XVIII. 2403.

The first of these reactions may account for the free acid which is obtained, as above mentioned, by the action of dilute alkalies on the raw product. Unchanged anhydride would, however, give the same result, and it is quite possible that appreciable quantities thereof may easily have been retained in the black residue after its treatment with benzol, owing to its gummy vitreous nature.

II. *Action of Phosphorpentoxide upon Metanitrobenzoic Anhydride in an Excess of Benzol.*

6 grams of metanitrobenzoic anhydride, m.pt. 161°, prepared by boiling a benzol solution of the acid with phosphorpentoxide, were heated in a sealed tube with 5 grams phosphoric anhydride, and 25–30 c.c. pure dry benzol for about four hours at 190–200°. After the reaction was completed, the contents of the tube consisted of a hard black vitreous residue, and a brownish supernatant liquid. This last was poured off, the residue washed several times with clean benzol, and the washings added to the decanted portion. The liquid was then purified by means of bone-black, and, after concentration, threw down a precipitate of fine white needles which, by their melting point, 161°, and ready solubility in alkalies, were easily identified as metanitrobenzoic anhydride.

The black vitreous residue from the benzol mother liquor was pulverized, freed from benzol as completely as possible by pressing between filters, and then extracted, first with potash to remove possible traces of acid and anhydride, then by repeated boiling with absolute alcohol. The dark red alcoholic extract gave, after treatment with bone-black and concentrating, a deposit of dark brown prismatic crystals, melting at 89°. By repeated crystallization from absolute alcohol these were finally obtained pure in the form of grayish white scales or leaflets, melting at 94–95°. The analyses gave the following values: —

0.2086 gr. substance gave 0.5248 gr. CO_2 and 0.0809 gr. H_2O.
0.2044 gr. substance gave 10.4 c.c. nitrogen gas at 10°.4 and 757.3 mm.

	Calculated for $C_6H_4\begin{cases}(1)\ NO_2\\(3)\ COC_6H_5.\end{cases}$	Found.
C	68.72	68.60
H	3.97	4.30
N	6.17	6.06

The substance is obviously metanitrobenzophenone, and its formation may be ascribed to reactions analogous to those above given for the corresponding ortho compound. The yield is much better than in the case of the ortho body, and its purification is a comparatively simple operation. It is insoluble in water, easily soluble in hot alcohol, benzol, and chloroform. Ether also dissolves it readily. Absolute alcohol is the best medium for its crystallization.

III. *Action of Phosphorpentoxide upon Paranitrobenzoic Anhydride in an Excess of Benzol.*

4.5 grams paranitrobenzoic anhydride, m.pt. 184°, prepared from the acid and phosphoric anhydride, were heated in a sealed tube with 5 grams phosphorpentoxide and 30–35 c.c. pure dry benzol at 190–200° for about four hours. As with the ortho and meta anhydrides, the product of the reaction consisted of two portions, a solid black deposit, and a more or less dark-colored supernatant liquid. The latter gave, after purification and concentration, a precipitate of anhydride, easily identified by its crystal form and melting point.

The residue was worked up in the same manner as described under the ortho and meta compounds. The chief product consisted of yellowish white scales melting at 137–138°, and, as the analyses prove, is paranitrobenzophenone.

0.2408 gr. gave 0.6081 gr. CO_2 and 0.0902 gr. H_2O.

0.1944 gr. gave 10.2 c.c. nitrogen at 16°.4 and 749.3 mm.

	Calculated for $C_6H_4\left\{\begin{array}{l}(1)\ NO_2\\(4)\ COC_6H_5.\end{array}\right.$	Found.
C	68.72	68.87
H	3.97	4.16
N	6.17	6.02

Paranitrobenzophenone crystallizes from hot absolute alcohol in yellowish scales. It is readily soluble in ether, chloroform, ligroine, benzol, and carbon disulphide, insoluble in water.

The course of the reaction by which the substance is formed is obviously the same as in the case of the isomeric ortho and metanitrophenones. The yield is much the best of the three, the raw product is less gummy, and the quantity of anhydride recovered from the benzol mother-liquor, very small. Traces of free acid are nevertheless present in the alkali washings, so that the possibility of the formation of the paranitrophenone by the first of the reactions above given cannot be entirely excluded.

CHLOR AND BROMBENZOPHENONES.

After we had succeeded in effecting the synthesis of the nitrophenones from the anhydrides, as above described, we concluded to extend the research to the corresponding halogen bodies. We found that, with the exception of the orthobrom derivative, the reaction takes place in precisely the same manner.

Orthobrombenzoic anhydride, prepared as stated in the previous paper, was heated in a sealed tube with an equivalent amount of phosphorpentoxide, and a considerable excess of benzol for four to five hours at 190 to 200°. The product was worked up as described under the nitrophenone, but without result. We were unable to obtain even a trace of brombenzoic acid, the only tangible product being a very small quantity of a yellowish oil, which could not be brought to crystallization. The operation we have repeated with varying quantities of the different factors, and varying times of heating, but without success. It will be remembered, in this connection, that in the case of the orthonitrophenone the course of the reaction left much to be desired, though we finally succeeded in obtaining enough product for analysis.

Metabrombenzophenone.

This body was prepared from metabrombenzoic anhydride, m.pt. 97°, by heating it in a sealed tube with phosphorpentoxide and benzol, and working up the product as described under the nitro compound. It crystallizes from alcohol in colorless needles, which melt at 74°, and dissolve readily in ether, chloroform, and benzol, less easily in alcohol and ligroine. The analyses gave as follows : —

0.2009 gr. substance gave 0.4401 gr. CO_2 and 0.0661 gr. H_2O.
0.1939 gr. gave 0.1390 gr. AgBr.

	Calculated for $C_6H_4\left\{\begin{matrix}(1)\ Br\\(3)\ COC_6H_5\end{matrix}\right.$	Found.
C	59.77	59.75
H	3.45	3.66
Br	30.66	30.51

Parabrombenzophenone.

From parabrombenzoic anhydride, m.pt. 212–213°, by heating to 190–200° with phosphorpentoxide and benzol. Crystallizes from alcohol in glittering leaflets, melting at 77°. Readily soluble in alcohol, ether, benzol, chloroform, and ligroine. Analyses: —

0.2570 gr. substance gave 0.5619 gr. CO_2 and 0.0962 gr. H_2O.
0.1591 gr. gave 0.1133 gr. AgBr.

	Calculated for $C_6H_4\left\{\begin{matrix}(1)\ Br\\(4)\ COC_6H_5.\end{matrix}\right.$	Found.
C	59.77	59.62
H	3.45	4.16
Br	30.66	30.31

Orthochlorbenzophenone.

From orthochlorbenzoic anhydride, phosphorpentoxide, and benzol. Crystallizes from ligroine in large rhombic prisms which deliquesce slowly in the air, and melt at 40–41°. Readily soluble in alcohol, ether, chloroform, and benzol, less easily in ligroine. It is best purified by distillation over a free flame and subsequent recrystallization from ligroine. Analyses: —

0.1401 gr. gave 0.3695 gr. CO_2 and 0.0531 gr. H_2O.
0.1143 gr. gave 0.0750 gr. AgCl.

	Calculated for $C_6H_4\left\{\begin{matrix}(1)\ Cl\\(2)\ COC_6H_5.\end{matrix}\right.$	Found.
C	72.04	71.93
H	4.16	4.21
Cl	16.40	16.23

Metachlorbenzophenone.

Crystallizes from alcohol or benzol in fine needles, which melt at 83°. Easily soluble in alcohol, ether, chloroform, benzol, and ligroine. Analyses: —

0.2158 gr. substance gave 0.5681 gr. CO_2 and 0.0831 gr. H_2O.
0.2204 gr. gave 0.1450 gr. AgCl.

	Calculated for $C_6H_4\left\{\begin{matrix}(1)\ Cl\\(3)\ COC_6H_5.\end{matrix}\right.$	Found.
C	72.04	71.80
H	4.16	4.28
Cl	16.40	16.27

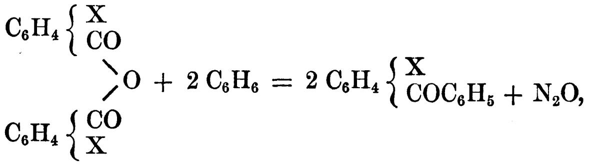
Parachlorbenzophenone.

From alcohol in leaflets melting at 78°. Readily soluble in alcohol, ether, benzol, chloroform, and ligroine. Analyses: —

0.2429 gr. substance gave 0.6439 gr. CO_2 and 0.0942 gr. H_2O.
0.1954 gr. gave 0.1280 gr. AgCl.

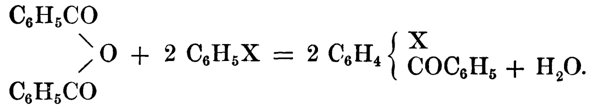
	Calculated for $C_6H_4\left\{\begin{matrix}(1)\ Cl\\(4)\ COC_6H_5.\end{matrix}\right.$	Found.
C	72.04	72.30
H	4.16	4.31
Cl	16.40	16.19

The results of our investigations show that the formation of acid anhydrides invariably precedes that of the phenones. In the case of the substituted derivatives two classes of reactions are possible; viz. the combination of substituted anhydrides with hydrocarbons:



$$\begin{matrix}C_6H_4\left\{\begin{matrix}X\\CO\end{matrix}\right.\\ \qquad\qquad>O\\ C_6H_4\left\{\begin{matrix}CO\\X\end{matrix}\right.\end{matrix} + 2\,C_6H_6 = 2\,C_6H_4\left\{\begin{matrix}X\\COC_6H_5\end{matrix}\right. + N_2O,$$

or benzoic anhydride with the substituted hydrocarbon:



$$\begin{matrix}C_6H_5CO\\ \qquad>O\\ C_6H_5CO\end{matrix} + 2\,C_6H_5X = 2\,C_6H_4\left\{\begin{matrix}X\\COC_6H_5\end{matrix}\right. + H_2O.$$

In the first instance the nature and position of the substituting radical appear to exercise a decided influence upon the course of the reaction. The orthobrom and orthonitro anhydrides react with difficulty, possibly owing to the formation of condensation or decomposition products between the adjacent side chains. Orthochlor anhydride reacts somewhat more readily. All the meta anhydrides give good yields of phenones; the para compounds, however, work best of all.

The essential conditions of the process appear to be, first, the presence of a negative radical in the acid anhydride; second, the farther this radical is removed from the carbonyl group the more complete will be the reaction.

By allowing phosphorpentoxide to react upon chlorbenzol and benzoic acid, or brombenzol and benzoic acid, Kollarits and Merz * have obtained a chlorbenzophenone (needles from ether-alcohol, m.pt. 75.5–76°), and a brombenzophenone (radiating forms, m.pt. 81°.5), probably identical with our parachlor and parabrom compounds above described. This would indicate that the carbonyl group of the acid anhydride assumes the para position with respect to the substituting negative radical of the hydrocarbon.

We have endeavored to carry out the same reaction, using nitrobenzol and metadinitrobenzol as substituting factors, but without result, notwithstanding our efforts to improve the course of the reaction by changing the amounts of materials employed and by heating at various temperatures.

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* Ber. d. ch. G., VI. 547.